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(54) **High ESCR glossy plastic containers**

(57) Plastic containers comprising two or more layers wherein the external or the internal layer consists essentially of a metallocene-produced medium density polyethylene resin, said plastic container having respec-

tively an external or internal gloss of at least 40 and an environmental stress crack resistance, as measured by the time to rupture, of at least 30 days.

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Description

[0001] This invention is related to polyethylene plastic containers having a very high environmental stress crack resistance, easy processing and a high gloss.

[0002] Several methods have been sought to produce high gloss plastic containers presenting good processability and good mechanical properties but all the blends and techniques used so far present various disadvantages.

[0003] High gloss high density polyethylene (HDPE) has been used: it is characterised by a very narrow molecular weight distribution that is typically inferior to 8. The molecular weight distribution can be completely defined by means of a curve obtained by gel permeation chromatography. Generally, the molecular weight distribution (MWD) is more simply defined by a parameter, known as the dispersion index D, which is the ratio between the average molecular weight by weight (Mw) and the average molecular weight by number (Mn). The dispersion index constitutes a measure of the width of the molecular weight distribution. It is known that a resin of narrow molecular weight distribution will produce plastic containers of very high gloss but simultaneously, that such resin will be very difficult to process and will be characterised by very poor mechanical properties. It has also been observed that said resins have poor mechanical properties, particularly, a very low environmental stress crack resistance (Modern Plastic International, August 1993, p. 45).

[0004] The coextrusion of high density polyethylene (HDPE) with a thin external layer of polyamide has been used to produce bottles of very high gloss but that method suffers the major drawback of necessitating an adhesive layer between the HDPE and the polyamide layers.

[0005] The coextrusion of high density polyethylene and an external layer of low density polyethylene leads to bottles with a fair gloss. These bottles however have an unpleasant greasy touch and offer a very poor resistance to scratching.

[0006] Metallocene-catalysed polyolefins have been used in transparent multilayer films suitable for packaging, for example in EP-A-756,931, WO-98-32601, WO-99-10430, WO-95-21743, WO-97-02294. None of these prior art documents has addressed the problem of this invention: the production of plastic container having a glossy outer surface.

[0007] In another method, disclosed in co-pending patent application, high gloss plastic containers comprise an internal layer including a polyolefin and an external layer including a styrenic component containing from 40 to 85 wt% of styrene, based on the weight of the external layer.

[0008] There is thus a need for a method for efficiently producing plastic containers of very high gloss as well as good processability and mechanical properties.

[0009] An aim of the present invention is to produce plastic containers that offer simultaneously the desired glossy appearance and a good resistance to scratching.

[0010] It is also an aim of the present invention to obtain glossy plastic containers with good processability and good mechanical properties.

[0011] It is a further aim of the present invention to prepare plastic containers having a very high environmental stress crack resistance.

[0012] It is another aim of the present invention to produce plastic containers having a very high melt fracture onset.

[0013] It is yet another aim of the present invention to produce a resin that can be utilised in coextrusion.

[0014] The present invention provides multi-layer plastic containers, wherein the external layer or the internal layer consists essentially of a metallocene-produced medium density polyethylene (mMDPE) having a density of from 0.925 to 0.940 g/cm³ and a melt index MI2 of from 0.5 to 2.5 g/10min, said plastic containers having an environmental stress crack resistance (ESCR), as measured by the time to rupture, larger than 30 days and respectively, an external or internal gloss larger than 40.

[0015] In this specification, the density of the polyethylene is measured at 23 °C using the procedures of ASTM D 1505 and the gloss was measured following the method of standard test ASTM D 2457-90. The time to rupture is measured on containers filled up to 98 % of their capacity with a 5 % concentrated Antarox as deteriorating agent. They are placed under a load of 10 kg at 40 °C. The time to rupture is recorded.

[0016] The melt index MI2 is measured using the procedures of ASTM D 1238 at 190°C using a load of 2.16 kg. The high load melt index HLMI is measured using the procedures of ASTM D 1238 at 190 °C using a load of 21.6 kg.

[0017] Preferably, the density of the mMDPE is of from 0.930 to 0.940 g/cm³.

[0018] The other layer(s) is(are) high density polyethylene(s) prepared with any one of the known catalysts, such as a chromium or a Ziegler-Natta or a metallocene catalyst, said metallocene catalyst being either the same as or different from the metallocene catalyst used to prepare the metallocene-produced external or internal layer.

[0019] According to a preferred embodiment of the present invention, the plastic containers are prepared by coextruding a metallocene-produced polyethylene resin and a high density polyethylene resin having a bimodal molecular weight distribution prepared with a Ziegler-Natta catalyst. The containers comprise from 10 to 30 wt% of the metallocene-produced polyethylene resin and from 90 to 70 wt% of the Ziegler-Natta high density polyethylene resin having a bimodal molecular weight distribution. The metallocene-produced resin can be used for the external layer if gloss is desired. Alternatively, it can be used for the internal layer. In addition, the on-line regrind made of bottle scraps is added

to the HDPE layer(s).

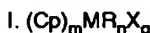
[0020] According to another embodiment of the present invention, the plastic containers are prepared by coextruding a metallocene-produced polyethylene resin and a high density polyethylene resin having a monomodal molecular weight distribution prepared with a chromium catalyst.

[0021] A number of different catalyst systems have been disclosed for the manufacture of polyethylene, in particular medium-density polyethylene (MDPE) and high-density polyethylene (HDPE) suitable for blow moulding. It is known in the art that the physical properties, in particular the mechanical properties, of a polyethylene product vary depending on what catalytic system was employed to make the polyethylene. This is because different catalyst systems tend to yield different molecular weight distributions in the polyethylene produced

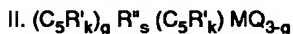
[0022] It is known in the art to use chromium-based catalysts to polymerise HDPE and in particular to produce high-density polyethylene having high resistance to environmental stress cracking. For example, EP-A-0,291,824, EP-A-0,591,968 and US-A-5,310,834 each disclose mixed catalyst compositions, incorporating chromium-based catalysts, for the polymerisation of polyethylene.

[0023] Alternatively, the HDPE can be produced using a conventional Ziegler-Natta catalyst or a supported Ziegler-Natta catalyst comprising metallocene sites such as described in EP-A-0,585,512 or in EP-A-0,580,930. The polymerisation is carried out in two liquid-full loop reactors in series at a temperature of from 50 to 120 °C, preferably of from 60 to 110 °C, under an absolute pressure of from 1 to 100 bar, in the presence of a catalyst consisting of a transition metal component (component A) that is the reaction product of an organoaluminium compound with a titanium compound, an organoaluminium compound (component B), and optionally one or more electron donor(s). The average molecular mass is regulated with hydrogen: this process comprises carrying the polymerisation such that the introduction of the comonomer, if any, is carried out essentially in the first reactor, such that the hydrogen concentration is very low in the first reactor in order to form ethylene polymers having a HLM of from 0.01 to 5 g/10 min and such that a very high hydrogen pressure is maintained in the second reactor in order to form an ethylene polymer having a HLM higher than 5 g/10 min.

[0024] The HDPE can further be polymerised with a metallocene catalyst capable of producing a mono- or bi- or multimodal distribution, either in a two step process such as described for example in EP-A-0,881,237, or as a dual or multiple site catalyst in a single reactor such as described for example in EP-A-0,619,325. Any metallocene catalyst known in the art can be used in the present invention. It is represented by the general formula:



wherein Cp is a cyclopentadienyl ring, M is a group 4b, 5b or 6b transition metal, R is a hydrocarbyl group or hydrocarboxy having from 1 to 20 carbon atoms, X is a halogen, and m=1-3, n=0-3, q=0-3 and the sum m+n+q is equal to the oxidation state of the metal.



wherein $(C_5R'_k)$ is a cyclopentadienyl or substituted cyclopentadienyl, each R' is the same or different and is hydrogen or a hydrocarbyl radical such as alkyl, alkenyl, aryl, alkylaryl, or arylalkyl radical containing from 1 to 20 carbon atoms or two carbon atoms are joined together to form a C_4-C_6 ring, R'' is a C_1-C_4 alkylene radical, a dialkyl germanium or silicon or siloxane, or a alkyl phosphine or amine radical bridging two $(C_5R'_k)$ rings, Q is a hydrocarbyl radical such as aryl, alkyl, alkenyl, alkylaryl, or aryl alkyl radical having from 1-20 carbon atoms, hydrocarboxy radical having 1-20 carbon atoms or halogen and can be the same or different from each other, Q' is an alkylidene radical having from 1 to about 20 carbon atoms, s is 0 or 1, g is 0, 1 or 2, s is 0 when g is 0, k is 4 when s is 1 and k is 5 when s is 0, and M is as defined above.

[0025] The metallocene may be supported according to any method known in the art. In the event it is supported, the support used in the present invention can be any organic or inorganic solids, particularly porous supports such as talc, inorganic oxides, and resinous support material such as polyolefin. Preferably, the support material is an inorganic oxide in its finely divided form.

[0026] An active site must be created by adding a cocatalyst having an ionising action.

[0027] Preferably, alumoxane is used as cocatalyst during the polymerization procedure, and any alumoxane known in the art is suitable.

The preferred alumoxanes comprise oligomeric linear and/or cyclic alkyl alumoxanes represented by the formula :

(IV) $R-(Al-O)_n-AlR_2$ for oligomeric, linear alumoxanes



and

(V) $(-Al-O-)_m$ for oligomeric, cyclic alumoxanes,



wherein n is 1-40, preferably 10-20, m is 3-40, preferably 3-20 and R is a C_1-C_8 alkyl group and preferably methyl. Methylalumoxane is preferably used.

[0028] When alumoxane is not used as a cocatalyst, one or more aluminiumalkyl represented by the formula AlR_x are used wherein each R is the same or different and is selected from halides or from alkoxy or alkyl groups having from 1 to 12 carbon atoms and x is from 1 to 3. Especially suitable aluminiumalkyl are trialkylaluminium, the most preferred being triisobutylaluminium (TIBAL).

[0029] The polymerisation of ethylene with the metallocene catalyst can be carried out in gas, solution or slurry phase. Preferably, the polymerization process is conducted under slurry phase polymerization conditions. The polymerisation temperature ranges from 20 to 125°C, preferably from 60 to 95°C and the pressure ranges from 0.1 to 5.6 Mpa, preferably from 2 to 4 Mpa, for a time ranging from 10 minutes to 4 hours, preferably from 1 and 2.5 hours.

[0030] It is preferred that the polymerization reaction be run in a diluent at a temperature at which the polymer remains as a suspended solid in the diluent.

[0031] A continuous loop reactor is preferably used for conducting the polymerisation.

[0032] The average molecular weight is controlled by adding hydrogen during polymerisation. The relative amounts of hydrogen and olefin introduced into the polymerisation reactor are from 0.001 to 15 mole percent hydrogen and from 99.999 to 85 mole percent olefin based on total hydrogen and olefin present, preferably from 0.2 to 3 mole percent hydrogen and from 99.8 to 97 mole percent olefin.

[0033] The density of the polyethylene is regulated by the amount of comonomer injected into the reactor; examples of comonomer which can be used include 1-olefins butene, hexene, octene, 4-methyl-pentene, and the like, the most preferred being hexene. The melt index of polyethylene is regulated by the amount of hydrogen injected into the reactor.

[0034] The polyethylene resin used in the present invention can be prepared with either a single site metallocene catalyst or with a multiple site metallocene catalyst and it has therefore either a monomodal or a bimodal molecular weight distribution. The molecular weight distribution is of from 2 to 20, preferably, of from 2 to 7 and more preferably of from 2 to 5.

[0035] The external or internal layer of the plastic containers is prepared with a metallocene-produced medium density polyethylene (mMDPE). Among the preferred metallocene catalysts used to prepare said external or internal layer, one can cite ethylene bis-(tetrahydroindenyl) zirconium dichloride, ethylene bis-(indenyl) zirconium dichloride and bis-(n-butyl-cyclopentadienyl) zirconium dichloride as disclosed for example in WO 96/35729. The most preferred metallocene catalyst is ethylene bis-(tetrahydroindenyl) zirconium dichloride because it allows the largest selection of densities, molecular weights and melt flow indices.

[0036] The densities of the polyethylenes required for preparing the external or internal layer of the plastic containers of the present invention range from 0.925 g/cm³ to 0.940 g/cm³ and preferably, from 0.930 to 0.940 g/cm³. The melt indices useful in the present invention range from 0.5 g/10' to 2.5 g/10' and the molecular weight distribution is of from 2 to 7, preferably from 2 to 5 and most preferably of less than 3.

[0037] The metallocene-produced medium density polyethylene resin (mMDPE) and the high density polyethylene resin (HDPE) are then coextruded to produce parisons that are blow-moulded into plastic containers having good physical and optical properties. In addition the containers of the present invention have a remarkable environmental stress crack resistance and are easy to process. They further have an excellent melt fracture onset in shear rate.

[0038] They are more preferably used for producing cosmetic packaging and household packaging such as detergent packaging of a capacity ranging from 0.01 to 20 litre.

[0039] The blow moulding machine, incorporating a coextrusion die for extruding a parison to be blow moulded, can be any one of the machines generally used for blow moulding. The following have been used for processing the polyethylene:

- a Battenfeld Fisher VK1-4 available from Battenfeld : this is a continuous extrusion or co-extrusion blow moulding machine with up to 6 extruders for the production of polyethylene bottles of 0.7 litre capacity, the bottles being either single layer or multi-layer with up to 6 layers;
- a high productivity wheel configuration machine with 6 cavities for continuous extrusion.

[0040] The plastic containers of the present invention are characterised by a very high gloss, as measured using the ASTM D 2457-90 test and an outstanding resistance to drop.

[0041] The drop resistance test is performed on 0.7-litre bottles prepared in accordance with the present invention.

[0042] The drop resistance is measured using the following procedure:

- rejection of the test if the impact was equivocal or if the cap was leaky;

A. Preparation of the equipment and bottles:

- the die and pin of the blow moulding equipment was cleaned on the day of production of the bottles;
- the bottles had a fairly homogeneous thickness;
- the net weight of bottles was 60 g;
- the empty bottles were stored at room temperature for about 20 hrs;
- the bottles were then filled with fluid, closed and brought to the desired conditioning as follows:

- 1) room temperature, water, 24 +/- 3 hrs;
- 2) -18 °C, water + anti-freeze, 24 +/- 3 hrs;

B. A test run on a sample of 20 bottles included the following steps:

- definition of the zero height;
- selection of a starting height for the drop test;
- selection of a homogeneous step distance in order to ensure the use of at least three different heights for each bottle tested;
- recording of the result in a grid shown in Table I;
- modification of the height by subtracting or adding one step distance depending upon whether the bottle broke or not;
- after 14 bottles were tested,

- 1) the test was interrupted if the number of ruptures $N=7$;
- 2) the test was continued until $N=7$, if N was <7 ;
- 3) the test was continued until the number of non-ruptures is 7, if N was >7

- the calculation of the height of rupture H_F was then given by the formula

$$H_F = H_0 + [\Delta H (A/N - 0.5)]$$

wherein

- H_0 is the minimum height,
- ΔH is the step distance,
- A is given by the product $(i * n_i)$ wherein n_i represents the number of ruptures at each height considering only the last 7 ruptures and i is an integer 0, 1, 2, ... indicating the number of steps above the minimum height H_0 ,
- N is the total number of ruptures.

[0043] In all the tests performed either on the resins of the present invention or on the comparative resins, the bottles were dropped from a maximum height of 6.5 m. No ruptures occurred ($n_i = 0$ and $i * n_i = 0$).

[0044] It is possible to produce coextruded plastic containers wherein the external layer is a metallocene-produced polyethylene resin and the internal layer is a high density polyethylene resin with a bimodal molecular weight distribution produced with a Ziegler-Natta catalyst. The external layer represents from 10 to 30 % by weight, preferably about 15 % by weight, of the total weight of the container.

[0045] The typical weight of the container can be reduced by as much as 30 to 40 % if so desired because of the excellent environmental stress crack resistance of the metallocene-produced resin.

[0046] Additionally and quite surprisingly, the production rate is very high even though the melt index is low.

5 Examples.

[0047] Several plastic containers were prepared and tested for gloss, ESCR, stacking under load and melt fracture onset in shear rate. They were prepared with the following resins.

10 [0048] Resin R1 is a metallocene-produced medium density polyethylene resin. It was obtained by continuous polymerisation in a loop slurry reactor with a supported and ionised metallocene catalyst prepared in two steps by first reacting SiO_2 with MAO to produce $\text{SiO}_2\cdot\text{MAO}$ and then reacting 94 wt% of the $\text{SiO}_2\cdot\text{MAO}$ produced in the first step with 6 wt% of ethylene bis-(tetrahydroindenyl) zirconium dichloride. The dry catalyst was slurried in isobutane and pre-contacted with triisobutylaluminium (TIBAl, 10 wt% in hexane) before injection in the reactor. The reaction was conducted in a 70 l capacity loop reactor with the polymerisation temperature being maintained at 85 °C. The operating conditions are as follows:

TIBAl: 120 cm^3/h

IC4: 26 kg/h

C2: 9 kg/h

20 C6: 50 cm^3/h

H2: 1.2 Nl/h.

[0049] Additionally, three high density polyethylene resins prepared with a Ziegler-Natta catalyst have been used:

- Resin R2 is Rigidex 4820 sold by BP Chemicals,
- Resin R3 is DSV 10305.00 sold by Dow Plastics, and
- Resin R4 is Finathene BM 593 produced by FINA Research S.A.

30 [0050] The characteristics of the four resins are summarised in Table I.

TABLE I.

Characteristics	R1	R2	R3	R4
HLMI g/10 min	25	52	49	26
MI2 g/10 min	0.85	1.70	1.00	0.27
Density g/cm^3	0.934	0.950	0.953	0.959
Bell ESCR F50 h	>1000	<24	43	250
GPC				
Mn	34083	19160	17690	12717
Mw	88134	102896	125473	170284
D	2.6	5.4	7.1	13.4

[0051] The Bell ESCR was measured following the method of standard test ASTM D 1690 and the HLMI was measured following the method of standard test ASTM 1238 at 190 °C and under a load of 21.6 kg.

50 [0052] These resins were coextruded with the VK-14 Battenfeld extruder to prepare seven two-layer 700 ml bottles of different compositions. The inner and outer layer compositions and proportions are as described in Table II as well as the bottles characteristics. About 30 wt% of bottle scraps were incorporated in the inner layer of all the bottles. The bottle height was 213 mm for all samples.

[0053] The machine operating conditions were as follows. The machine output: is of about 15 kg/h and the mass temperature is of from 170 to 215 °C.

55 The die gap is progressively reduced by 100 steps in the machine setting, while keeping a constant output. The shear rate for melt fracture onset is recorded and the trial is stopped at that position.

[0054] The swell in weight (50 cm parison length) is recorded at positions 500 and 1000 of the die gap.

TABLE II.

Bottle	B1	B2	B3	B4	B5	B6	B7
Inner layer Resin	R4	R4	R4	R4	R4	R4	R4
Inner layer thickness %	70	70	70	70	85	85	85
Outer layer resin	R2	R1	R1	R1	R1	R1	R1
Outer layer thickness %	30	30	30	30	15	15	15
Mass temp. °C	213	208	210	210	210	211	209
Bottle thickness mm	0.7	0.7	0.85	1.0	0.7	0.85	1
Bottle weight g	41.2	38	47	54	38	47	54

[0055] The gloss was measured at an angle of 60 ° using the method of standard test ASTM D 2457-90.

[0056] The environmental stress crack resistance was measured on bottles filled up to 98 % of their capacity with a 5 % concentrated Antarox as deteriorating agent. They were then placed under a load of 10 kg at 40 °C. The test has now been prolonged for 10 weeks without showing any signs of rupture for all the bottles prepared according to the present invention.

[0057] The bottle deflection was measured after 48 hours of testing under the load of 10 kg at 40 °C.

[0058] The swell in weight of the plastic containers prepared according to the present invention has been reduced by 5 % with respect to mono-layer containers made of resin R4.

[0059] The results are displayed in Table III.

TABLE III.

Bottle	B1	B2	B3	B4	B5	B6	B7
Melt fracture onset s-1	1074	9500	9500	9500	9500	9500	9500
Ext. gloss %	58	90	90	90	90	90	90
Time to rupture Days	6.6	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.
Bottle deflection Mm	8	13.6	8.8	6.8	11.8	8.8	6.2

n.r. means no rupture after 70 days of testing.

[0060] Two 200 ml bottles were coextruded on a continuous five cavities machine with the following compositions:

- Bottle B8 was coextruded at a mass temperature of 170 °C: it comprised a 70 wt% inner layer prepared from the Dow 35060 E HDPE resin produced with a Ziegler-Natta catalyst and having a bimodal molecular weight distribution and a 30 wt% outer layer prepared from the Dow DSV 10305.00 MDPE resin R3;
- Bottle B9 was coextruded at a mass temperature of 170 °C with a 80 wt% inner layer prepared layer prepared from the Dow 35060 E HDPE resin and a 20 wt% outer layer prepared from the metallocene-produced MDPE resin R1.

[0061] These bottles were tested for melt fracture onset and external gloss. The results are displayed in table IV.

TABLE IV.

Bottle	B8	B9
Main temp. °C	170	170
Melt fracture onset s-1	1500	None
External gloss %	37	87

[0062] These examples clearly show that when the external layer of plastic containers is prepared from a metallocene-produced medium density polyethylene, the final product has an excellent processability as the metallocene resin is very little sensitive to melt fracture. They also have a very high external gloss and a highly improved environmental stress crack resistance. Structures having a very high ESCR potential can be prepared with a reduced weight

either with thinner walls or a higher density grade in the inner layer.

[0063] In addition, most coextruded structures available on the market generally have respectively a 70 % and 30 % composition for the inner and outer layers. The examples show that when the outer layer is made of a metallocene-produced medium density polyethylene an 85/15 coextruded composition has outstanding properties.

[0064] The containers produced according to the present invention are suitable for use in the cosmetic and detergent packaging.

Claims

1. A plastic container comprising two or more layers wherein the external or the internal layer consists essentially of a metallocene-produced medium density polyethylene (mMDPE) resin, said plastic container having respectively an external or internal gloss of at least 40 and an environmental stress crack resistance, as measured by the time to rupture, of at least 30 days.
2. A plastic container according to claim 1, wherein the metallocene-produced medium density polyethylene has a density of from 0.925 to 0.940 g/cm³ and a melt index MI2 of from 0.5 to 2.5 g/10min.
3. A plastic container according to claim 1 or claim 2 wherein the metallocene-produced medium density polyethylene has a molecular weight distribution of from 2 to 7.
4. A plastic container according to any one of the preceding claims wherein the metallocene-produced medium density polyethylene resin used in the external or internal layer represents from 10 to 30 wt% of the total weight of the container.
5. A plastic container according to any one of the preceding claims, consisting of two layers and wherein the external layer is a metallocene-produced medium density polyethylene and the internal layer is a Ziegler-Natta high density polyethylene resin having a bimodal molecular weight distribution.
6. A plastic container according to any one of the preceding claims that is produced by blow moulding a coextruded parison.
7. Cosmetic packaging produced according to any one of claims 1 to 5.
8. Detergent packaging produced according to any one of claims 1 to 5.



European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 01 20 3726

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
E	EP 1 138 702 A (FINA RESEARCH) 4 October 2001 (2001-10-04) * page 6, line 29 - page 7, line 31 * * claims 1-4,6-10 *	1-3,5-8	B32B27/32 B29C49/22 B65D1/00 C08F10/02 C08J5/18
Y	WO 97 06951 A (COUTANT WILLIAM R ; LAURIERS PAUL J DES (US); PALACKAL SYRIAC J (US) 27 February 1997 (1997-02-27) * page 24, line 1 - page 25, line 18 * * page 26; example II *	1-3	
Y	US 6 153 716 A (ALT HELMUT G ET AL) 28 November 2000 (2000-11-28) * column 11, line 1 - line 38 *	1-3	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			B32B B29C B65D C08F C08J
The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 26 February 2002	Examiner Lindner, T
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

EPO FORM 1503 03.02 (P04001)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
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26-02-2002

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
EP 1138702	A	04-10-2001	EP	1138702 A1	04-10-2001
			AU	5474901 A	08-10-2001
			WO	0172856 A1	04-10-2001
WO 9706951	A	27-02-1997	AU	702109 B2	11-02-1999
			AU	6770896 A	12-03-1997
			BR	9610302 A	06-07-1999
			CA	2229172 A1	27-02-1997
			CN	1193298 A ,B	16-09-1998
			EA	980206 A1	29-10-1998
			EP	0853549 A1	22-07-1998
			HU	9901500 A2	30-08-1999
			JP	11510849 T	21-09-1999
			NO	980629 A	13-02-1998
			PL	325051 A1	06-07-1998
			US	6214469 B1	10-04-2001
			WO	9706951 A1	27-02-1997
			US	6153716 A	28-11-2000
US 6153716	A	28-11-2000	US	5498581 A	12-03-1996
			AU	702109 B2	11-02-1999
			AU	6770896 A	12-03-1997
			BR	9610302 A	06-07-1999
			EA	980206 A1	29-10-1998
			EP	0853549 A1	22-07-1998
			JP	11510849 T	21-09-1999
			NO	980629 A	13-02-1998
			PL	325051 A1	06-07-1998
			US	6214469 B1	10-04-2001
			CA	2229172 A1	27-02-1997
			CN	1193298 A ,B	16-09-1998
			HU	9901500 A2	30-08-1999
			WO	9706951 A1	27-02-1997
			AT	164857 T	15-04-1998
			AT	189823 T	15-03-2000
			AU	677902 B2	08-05-1997
			AU	2011695 A	04-01-1996
			AU	686538 B2	05-02-1998
			AU	3156997 A	02-10-1997
			BG	99676 A	31-05-1996
			BR	9502632 A	30-04-1996
			CA	2143586 A1	02-12-1995
			CN	1117053 A ,B	21-02-1996
			CZ	9501389 A3	13-12-1995
			DE	69501977 D1	14-05-1998
			DE	69501977 T2	30-07-1998

EPC FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 01 20 3726

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

26-02-2002

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 6153716 A	DE	69515135 D1	23-03-2000
	DE	69515135 T2	15-06-2000
	DK	810234 T3	05-06-2000
	EP	0685495 A1	06-12-1995
	EP	0810234 A2	03-12-1997
	ES	2114248 T3	16-05-1998
	ES	2142124 T3	01-04-2000
	FI	952645 A	02-12-1995
	GR	3033150 T3	31-08-2000
	HU	72719 A2	28-05-1996
	JP	8059729 A	05-03-1996
	NO	952162 A	04-12-1995
	NO	5744 A	04-12-1995
	PL	308837 A1	11-12-1995
	SG	32355 A1	13-08-1996
	SK	71895 A3	06-12-1995
	ZA	9504144 A	19-01-1996

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82